

Intensified Flue Gas Desulfurization Water Treatment for Reuse, Solidification, and Discharge (DE-FE-0031555)

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Annual Project Review Meeting, April 11th, 2019

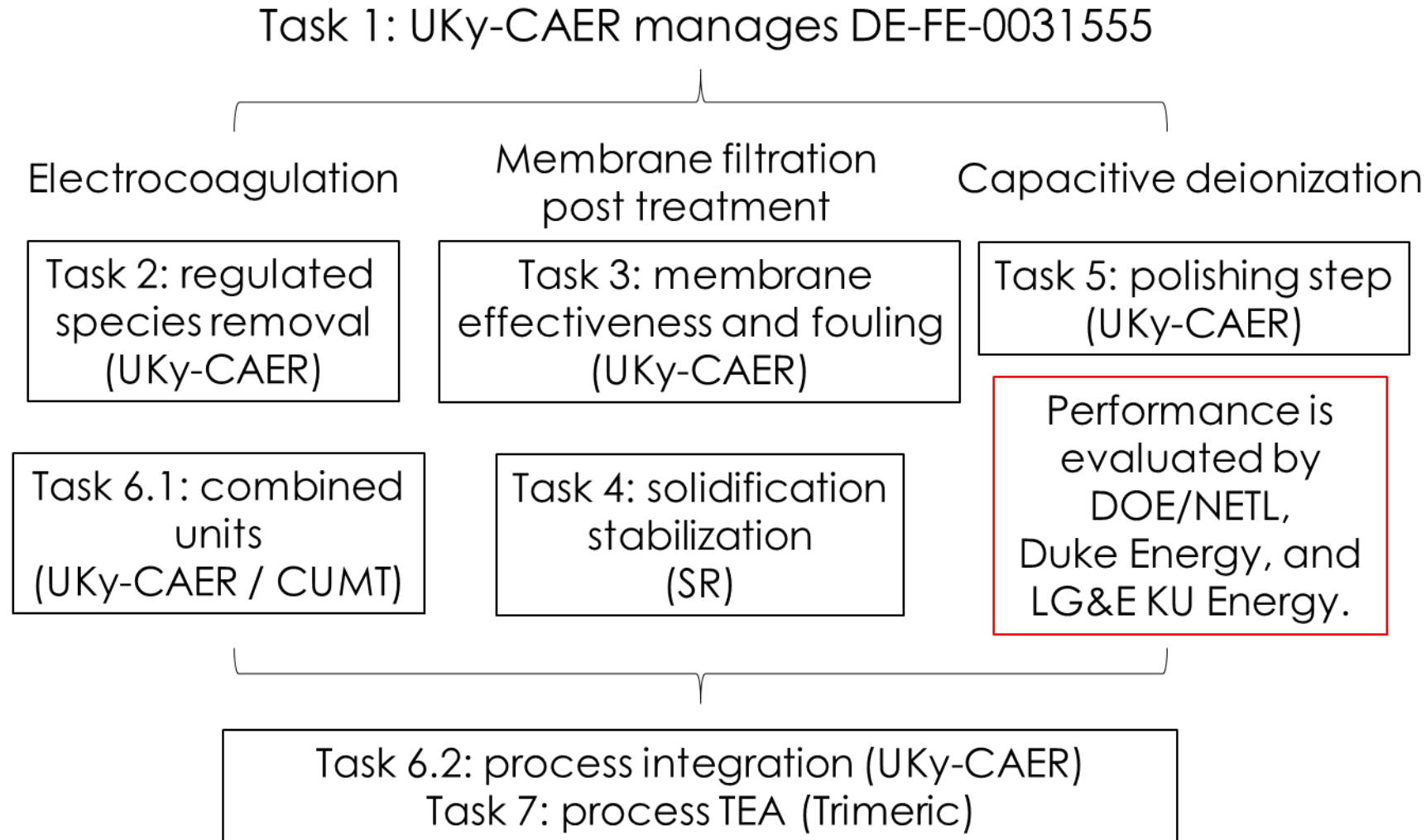
Project purpose

- Intensified process with less chemical use for FGD water discharge.
- Reducing freshwater intake for FGD processes.

Project objectives

- Electrocoagulation (EC) effectiveness on Se, As, and NO_3^- removal.
- Evaluating nanofiltration (NF) membranes to remove Cl^- and SO_4^{2-} .
- Developing methods to mitigate membrane fouling.
- Determining practical upper-limit salt concentrations for solidification towards an acceptable leachate including regulated species and soluble salts.
- Capacitive deionization (CDI) and zeolite effectiveness for other beneficial uses.

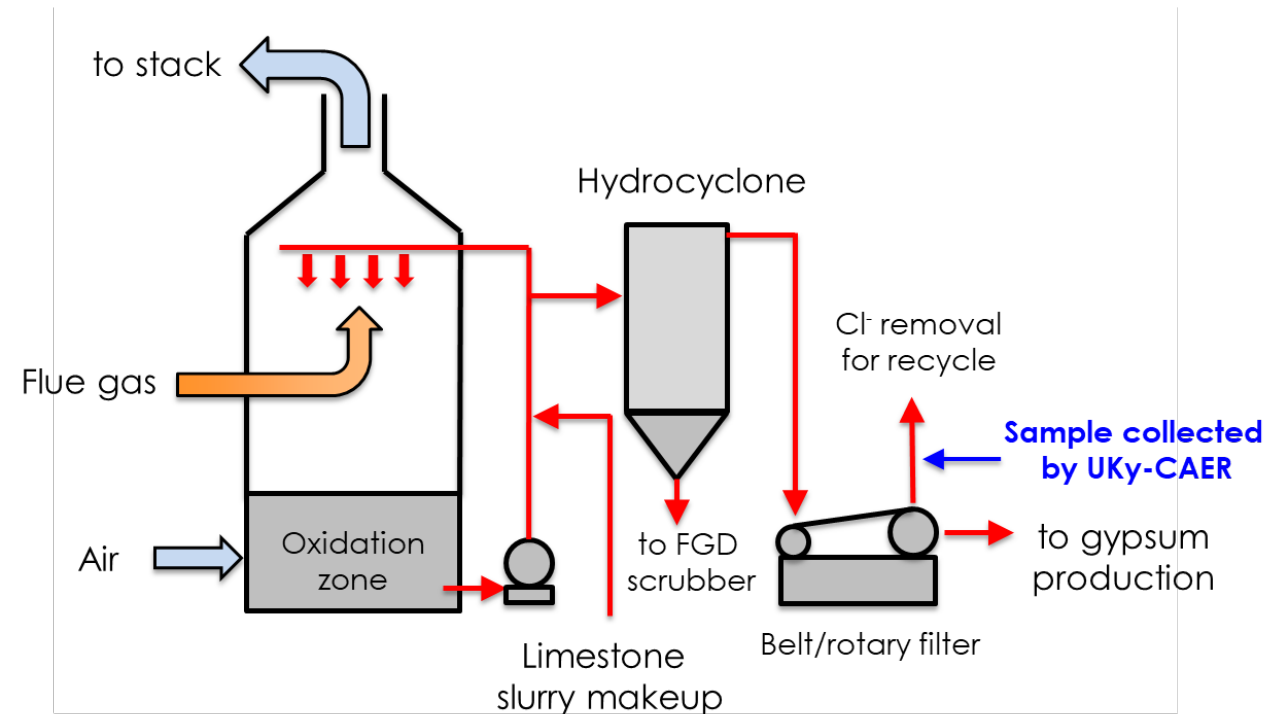
Project Team and Task Assignment



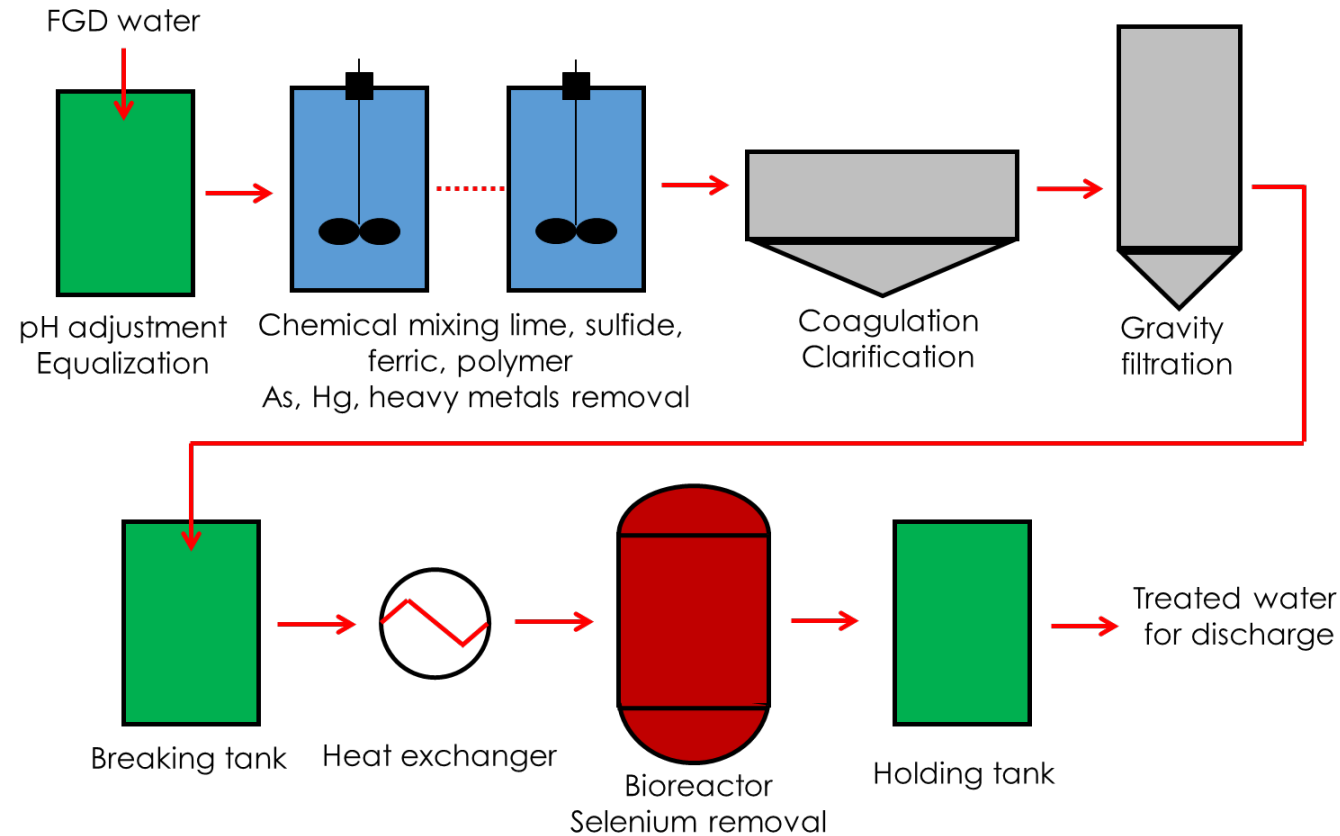
FGD water: high Cl^- and SO_4^{2-} with trace regulated species

- Coal-S $\xrightarrow{\text{combustion}}$ $\text{SO}_{2(g)}$ $\xrightarrow{\text{dissolve}}$ SO_3^{2-} $\xrightarrow{\text{oxidize}}$ SO_4^{2-}
- Coal-Cl $\xrightarrow{\text{combustion}}$ $\text{HCl}_{(g)}$ $\xrightarrow{\text{dissolve}}$ Cl^-
- Coal-Se $\xrightarrow{\text{combustion}}$ $\text{SeO}_{2(g)}$ $\xrightarrow{\text{dissolve}}$ SeO_3^{2-} $\xrightarrow{\text{oxidize}}$ SeO_4^{2-}

Species	Plant A	Plant B
SO_4^{2-}	8,100 ppm	1,100 ppm
Cl^-	5,500 ppm	11,000 ppm
Se	1200 ppb	330 ppb



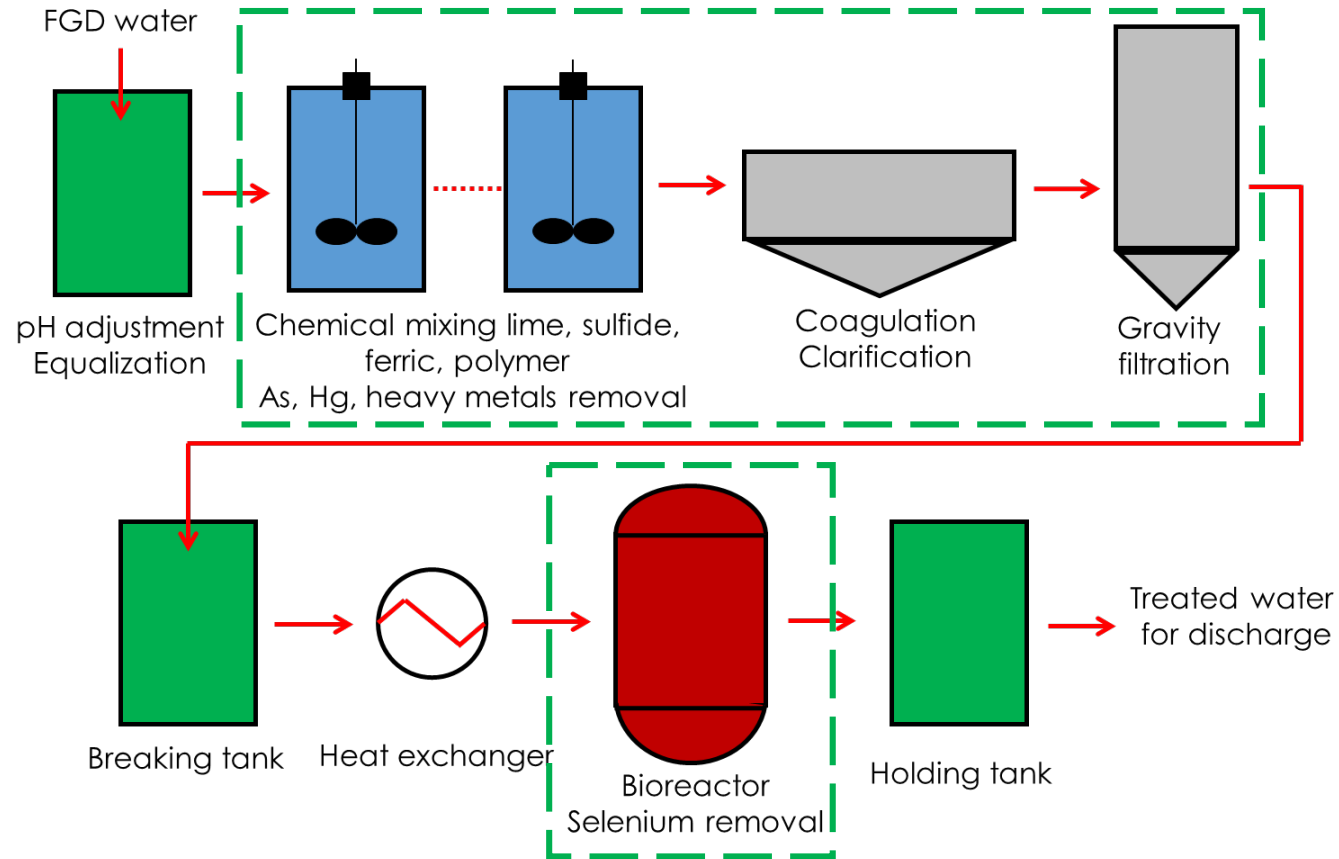
Current State-of-The-Art Technology for FGD Water Discharge



- Regulated species are removed by a multistep process with chemical additions and temperature control.

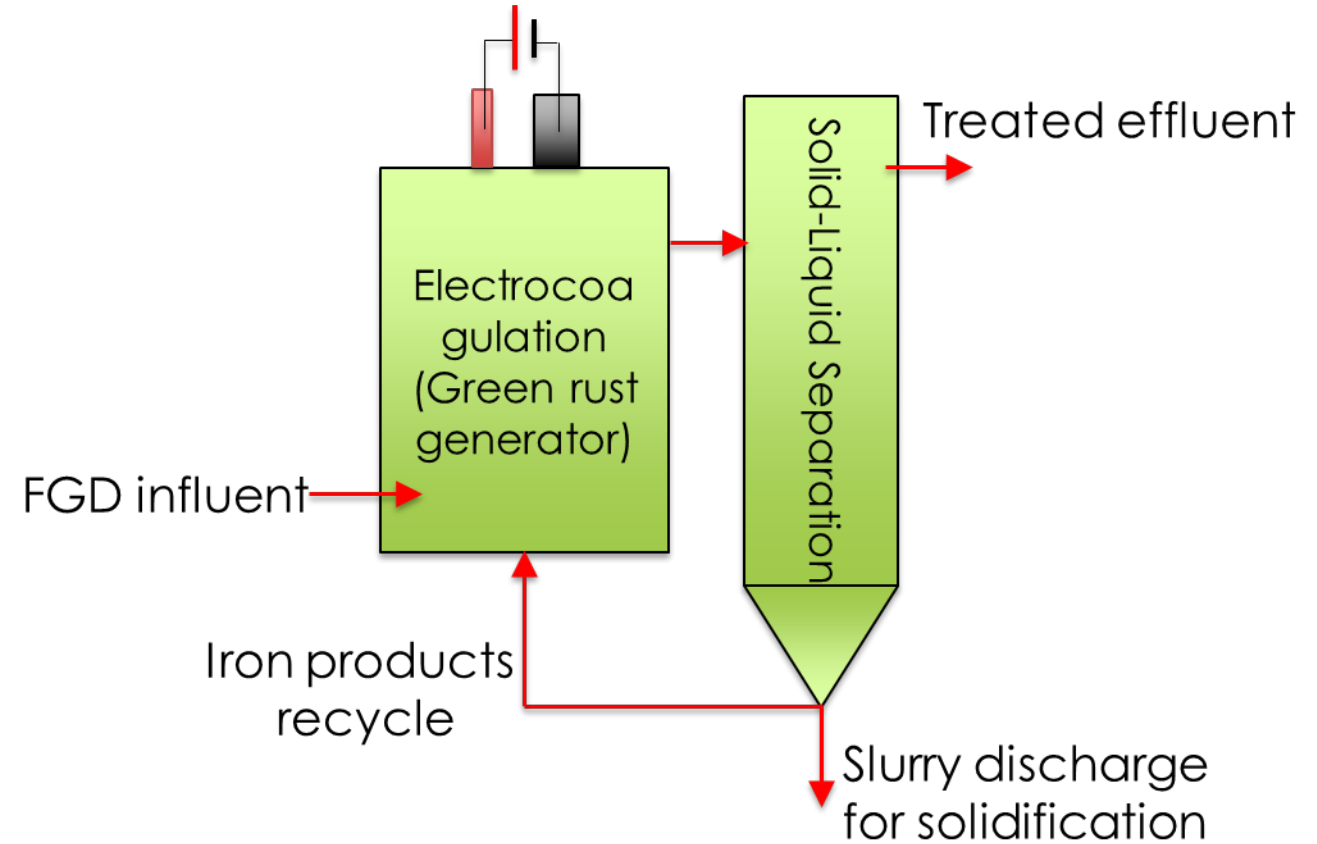
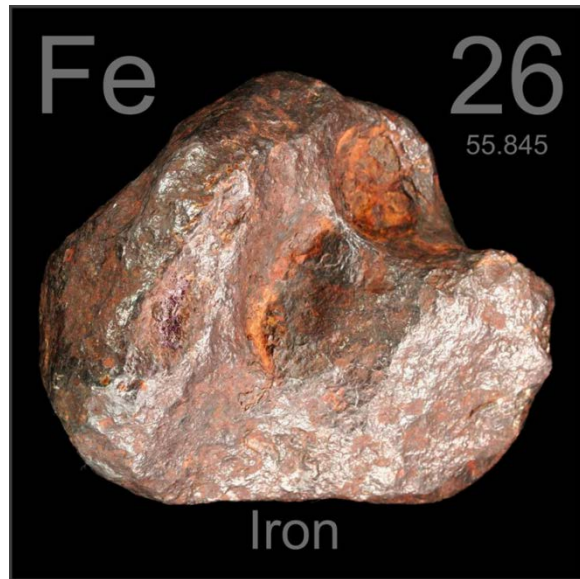
International Water Conference, Duke Energy Carolina LLC, Saint Antonio, TX (2008)

UKy-CAER Aims to Develop An Intensified Process.

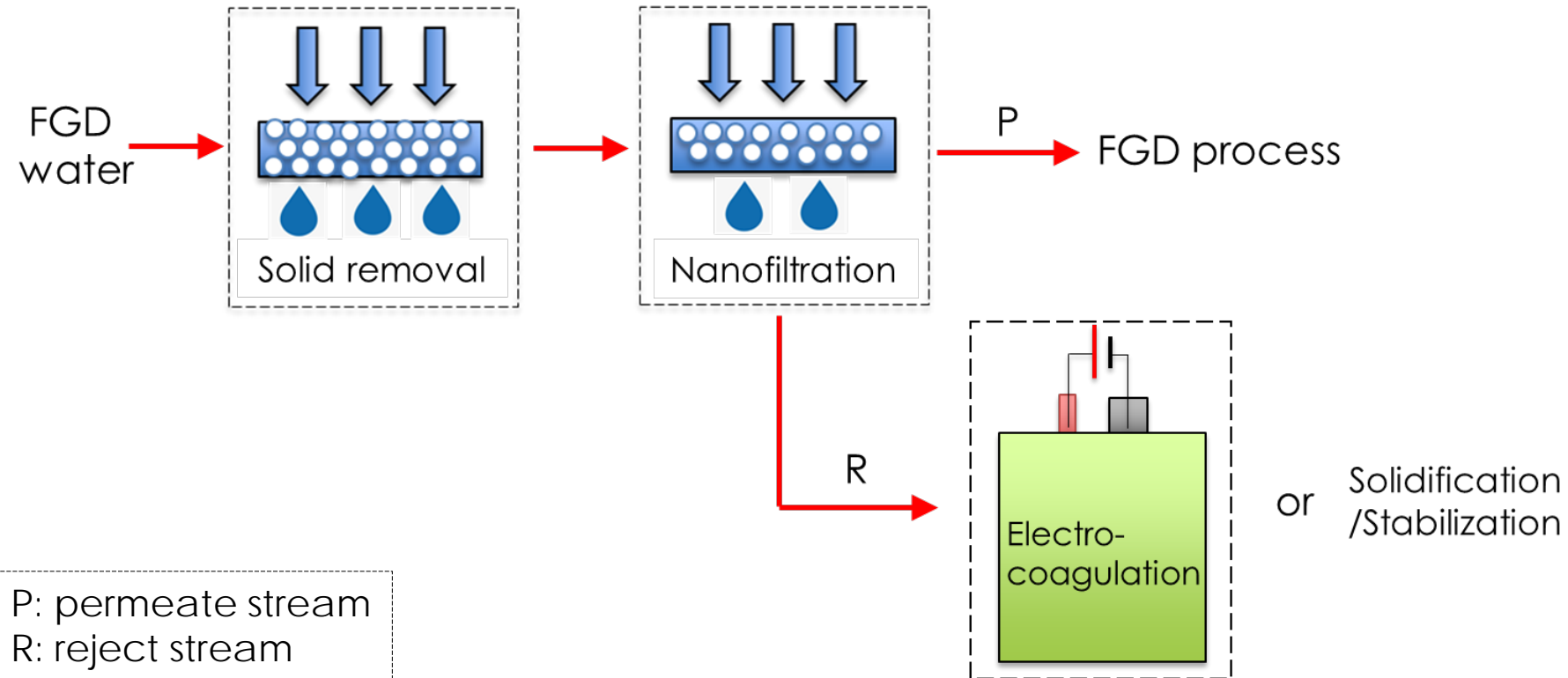


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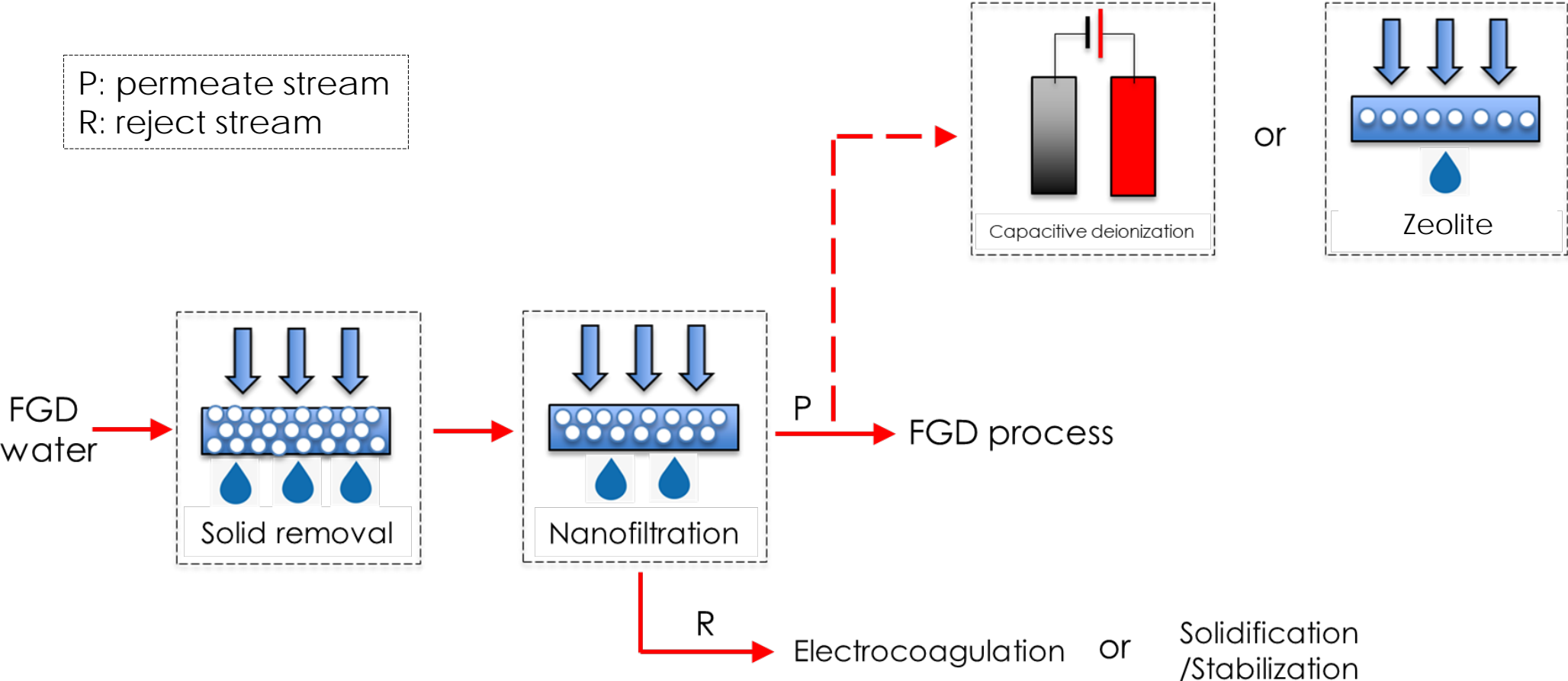
Approach: Regulated Species Removal



Approach: Reducing Freshwater Intake



Deep Cleaning for Beneficial Uses

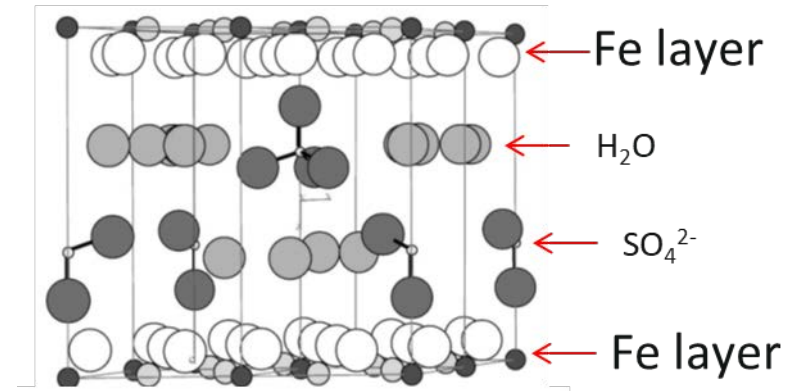


- Green rust, an iron-electrolysis product, selectively removed regulated species from FGD water in continuous operation, and demonstrated its effectiveness to meet the ELG's daily discharge limits. (project milestone)
- TS80, a commercially available NF membrane, can achieve >90% salt rejection and >80% water recovery for >50 hours using FGD water containing antiscalants. (project milestone)
- Capacitive deionization and zeolite filtration possessed excellent salt removal.
- Solidification/stabilization of NF reject is currently performed by Southern Research, especially looking at selenate and soluble salts leachate.

Utilizing High Cl^- and SO_4^{2-} to Prepare Green Rust



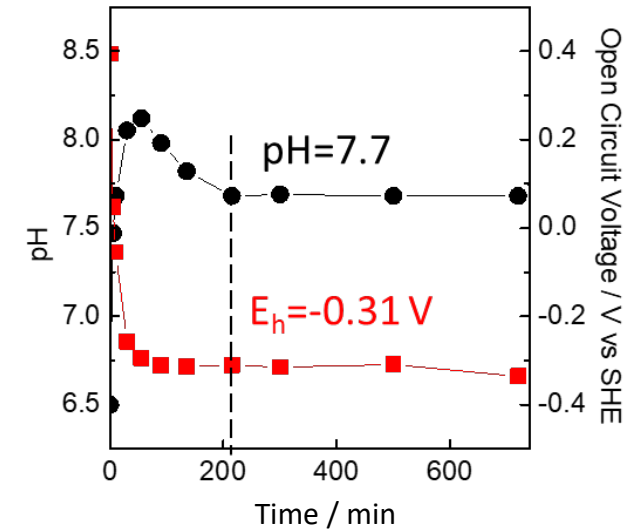
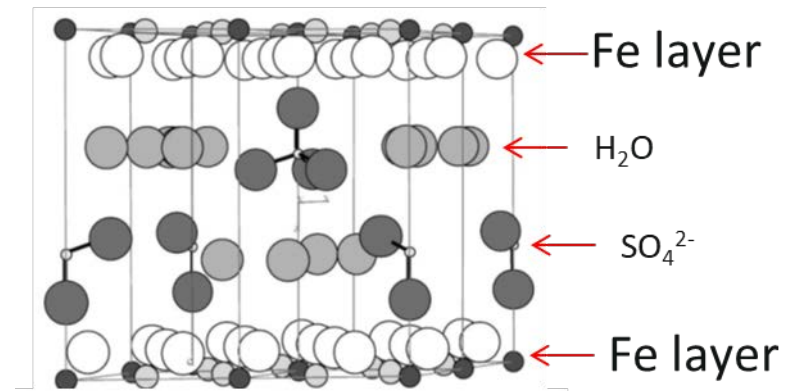
Batch setup



Utilizing High Cl^- and SO_4^{2-} to Prepare Green Rust



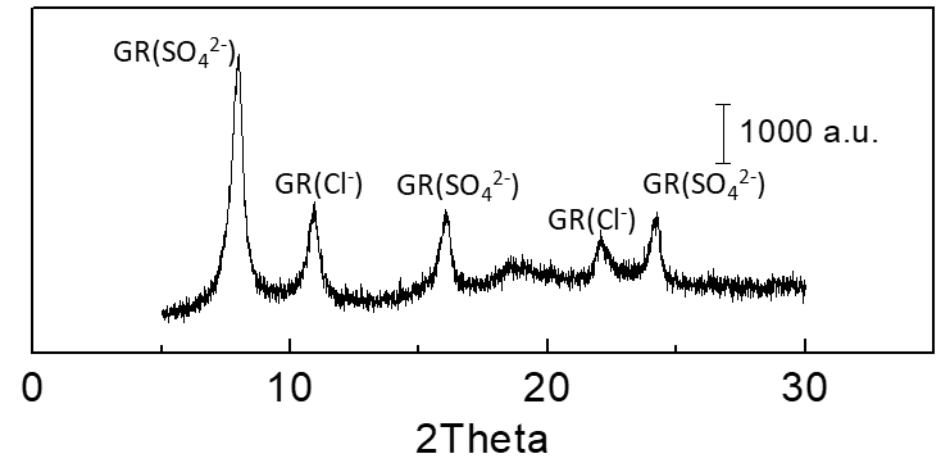
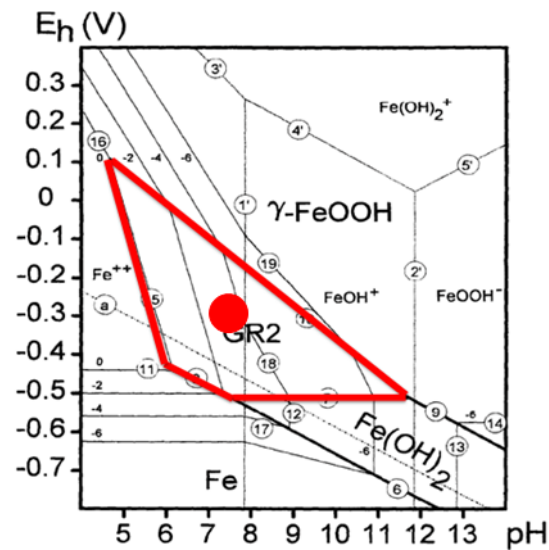
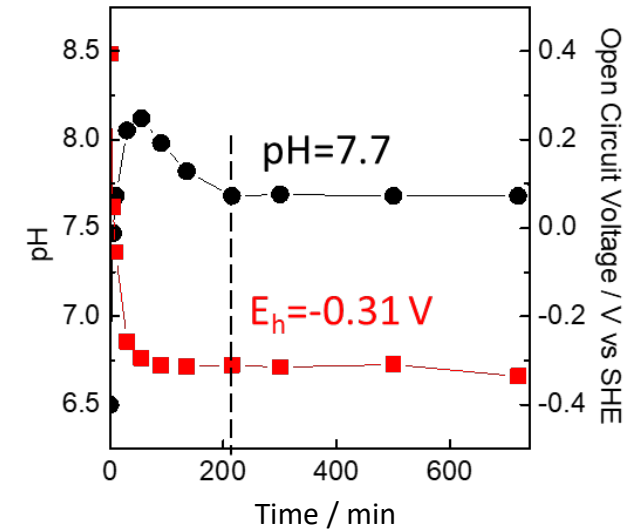
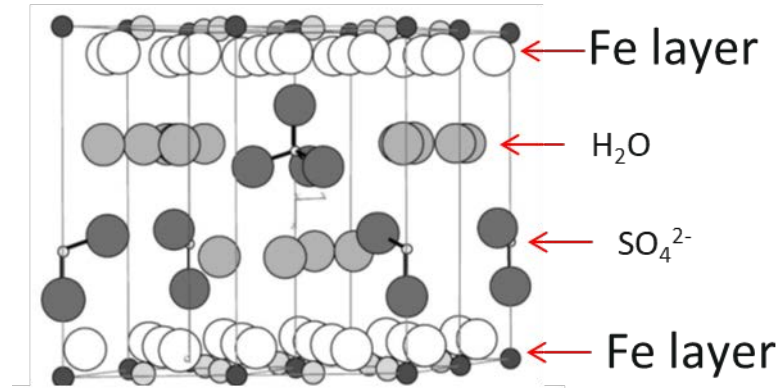
Batch setup



Utilizing High Cl^- and SO_4^{2-} to Prepare Green Rust

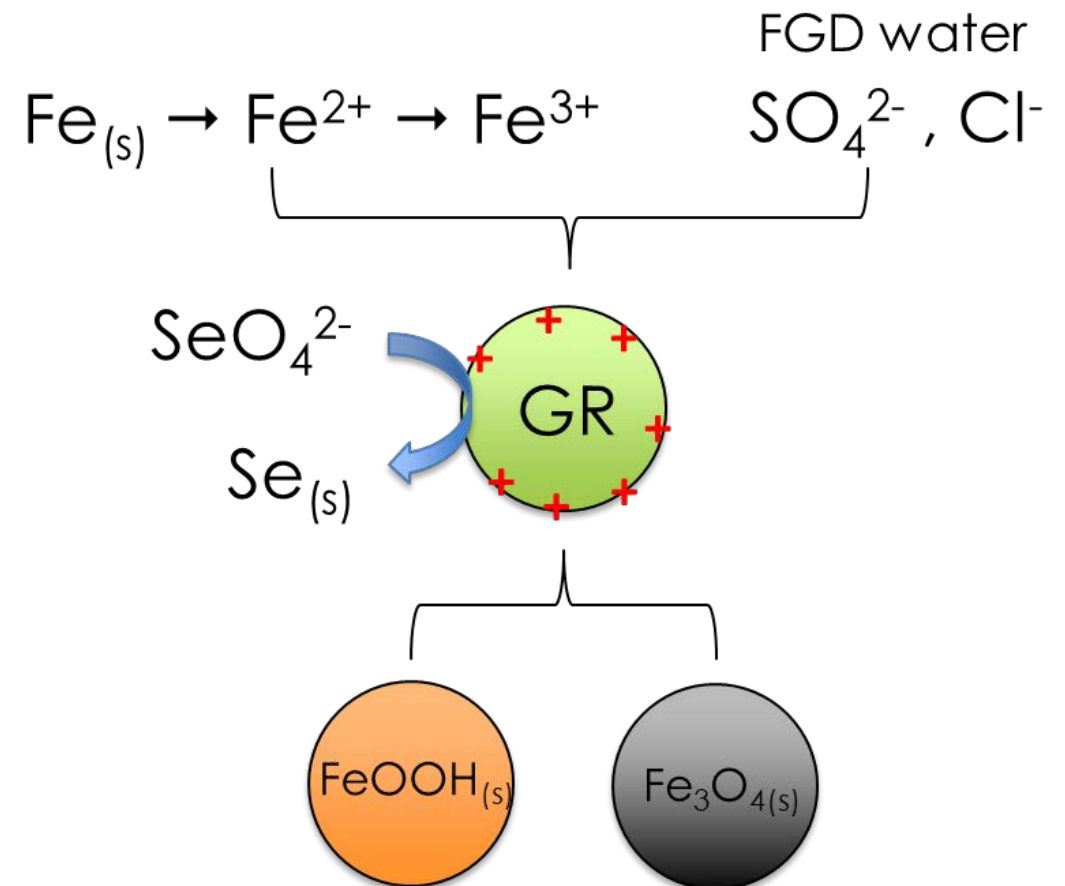


Batch setup

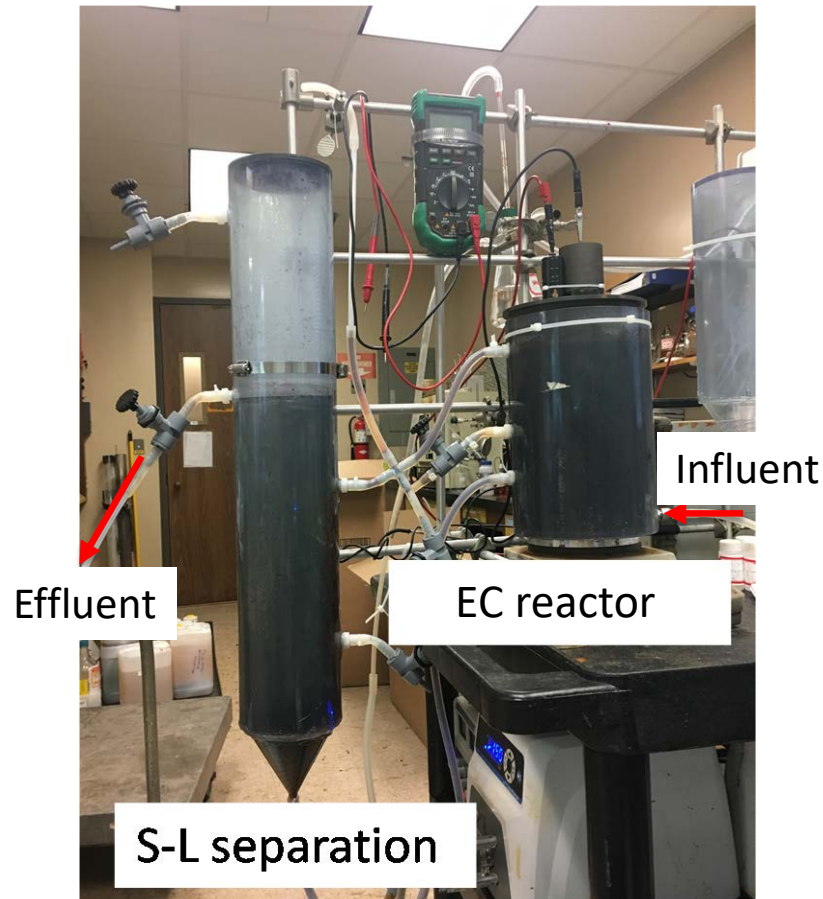


Mechanism of Regulated Species Reduced by GR in EC

- *Chem. Rev.*, 118, 3251 (2018)
 - Comprehensive review of GR and its environmental applications
- *Science*, 278, 1106 (1997), and *Environ. Sci. Tech.*, 34, 819 (2000)
 - Selenate
- *Environ. Sci. Tech.*, 30, 2053 (1996) and *Appl. Clay Sci.*, 18, 81 (2001)
 - Nitrate
- *Environ. Sci. Tech.*, 38, 5224 (2004)
 - Arsenic
- *Chemosphere*, 53, 437 (2003)
 - Silver, gold, copper, and mercury



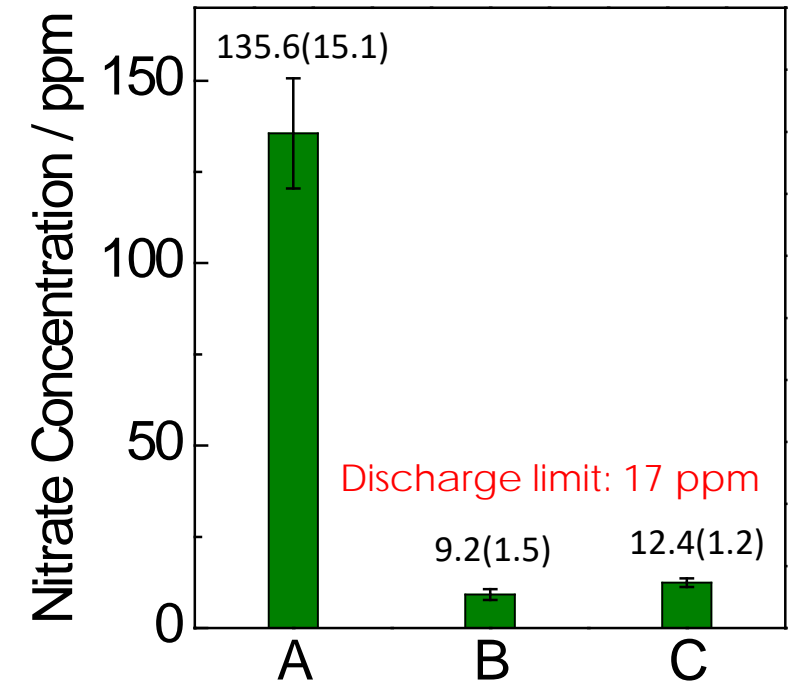
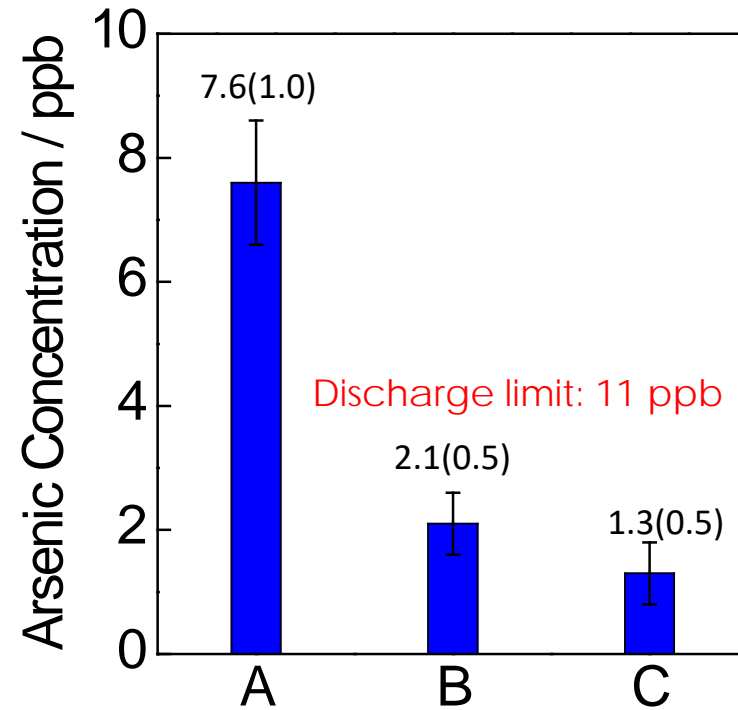
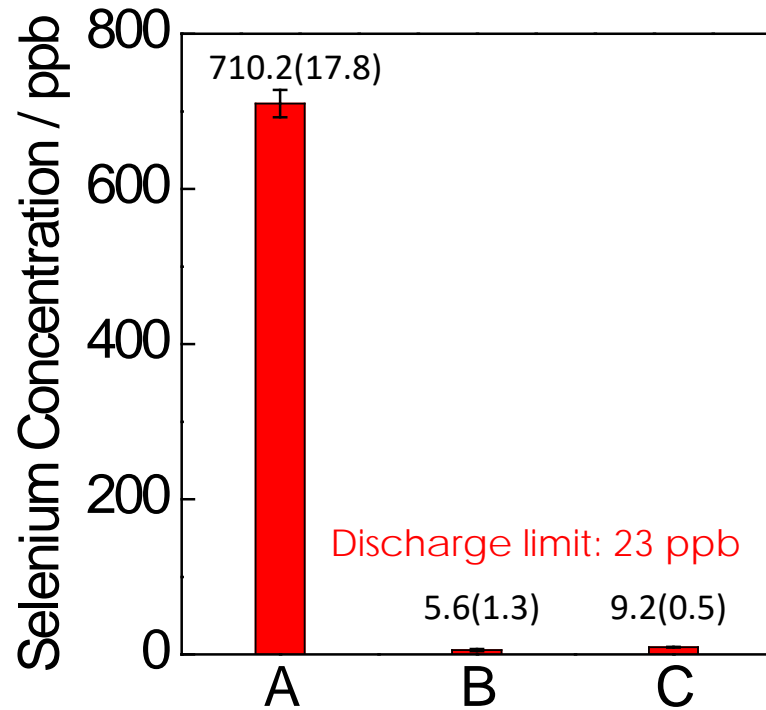
Intensified Process: Brief Introduction



Continuous operation

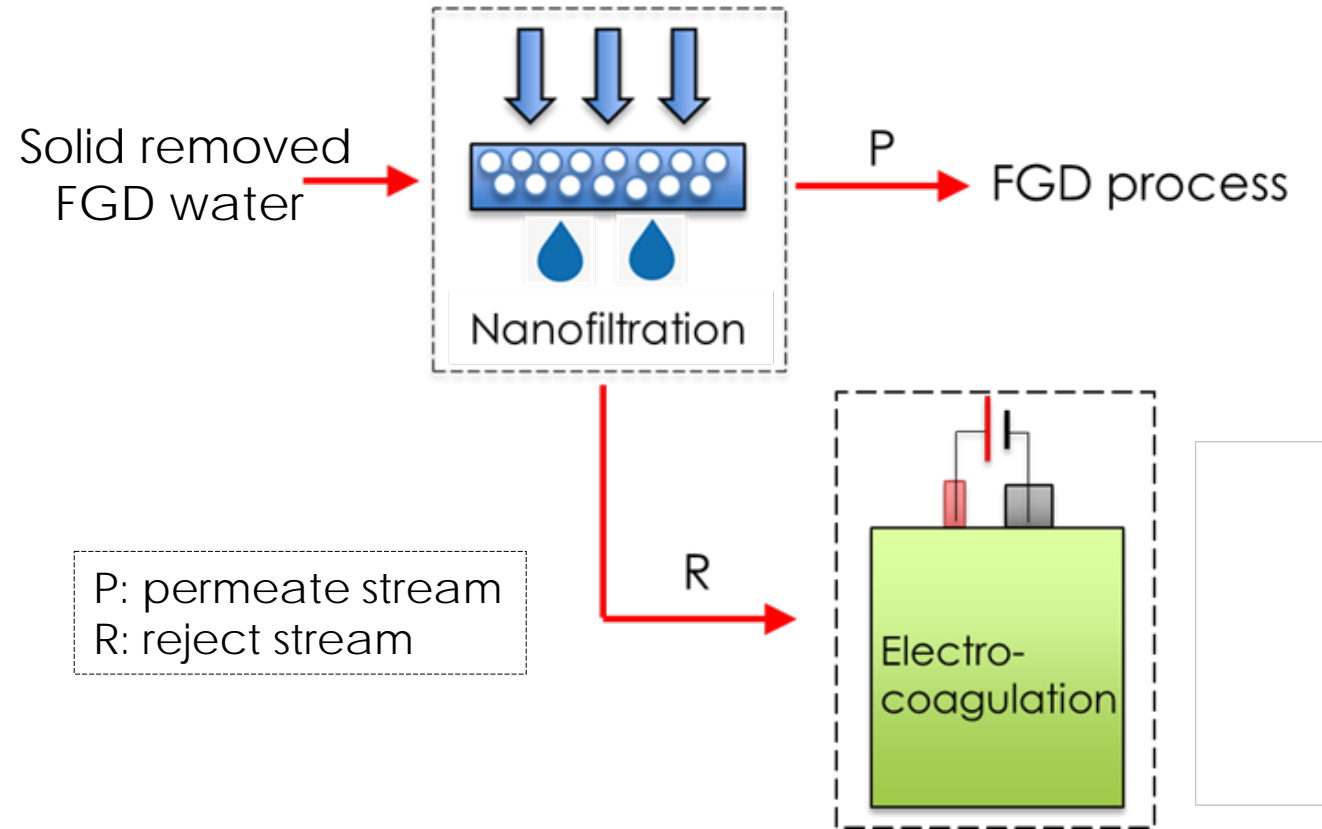
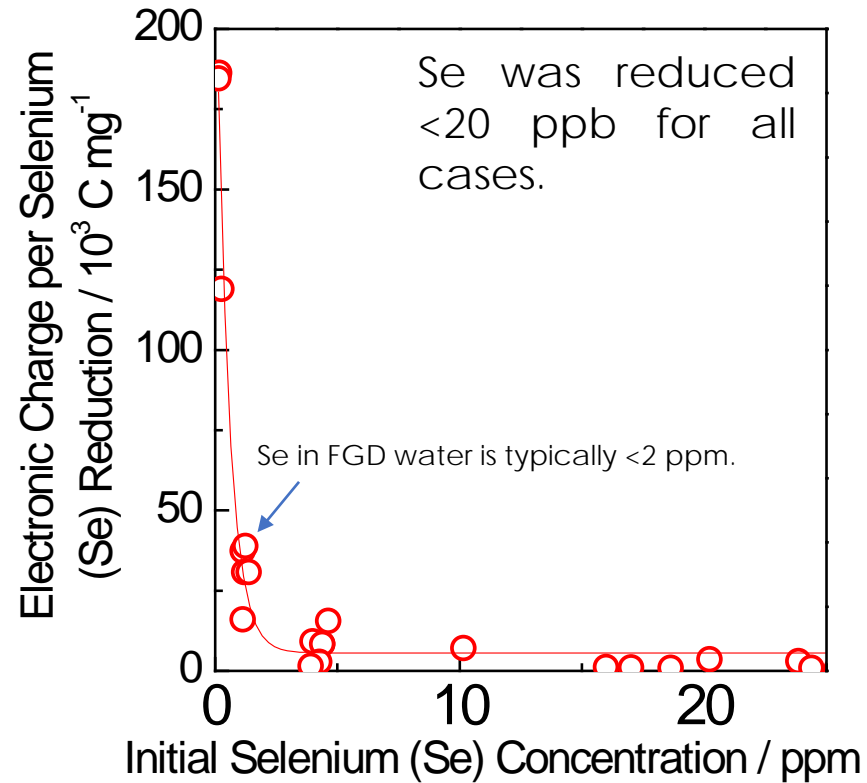
- GR is continuously produced in an EC reactor to remove regulated species.
- GR is settled by its gravity, and treated FGD effluent overflows.
- GR is partially recycled depending upon its effectiveness.

Effectiveness of Regulated Species Reduction



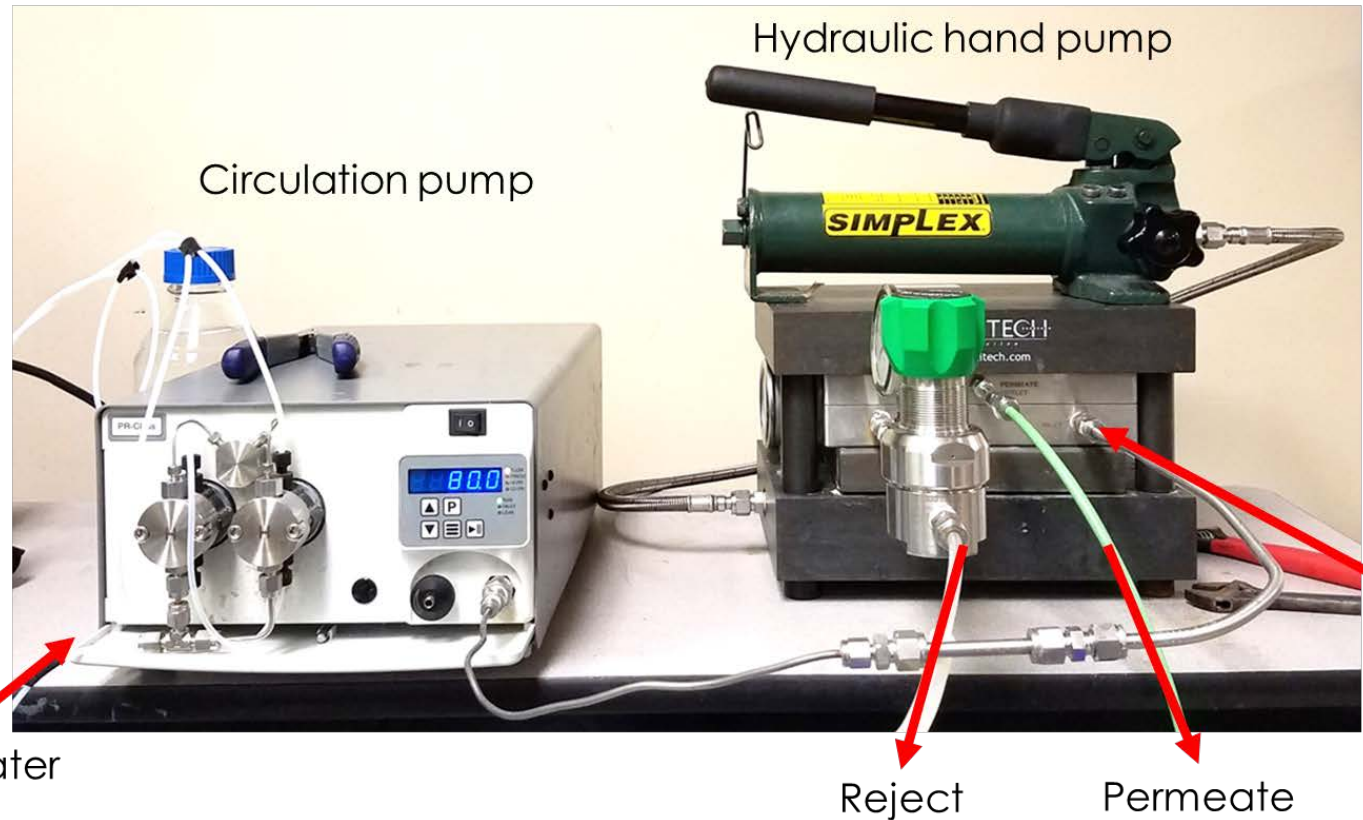
- A: starting FGD water, B: during operation, and C: after operation.
- Conditioning: 5 A for 4 hours, and continuous operation: 3 A at 30 mL min⁻¹

Additional Findings Facilitate Process Integration.



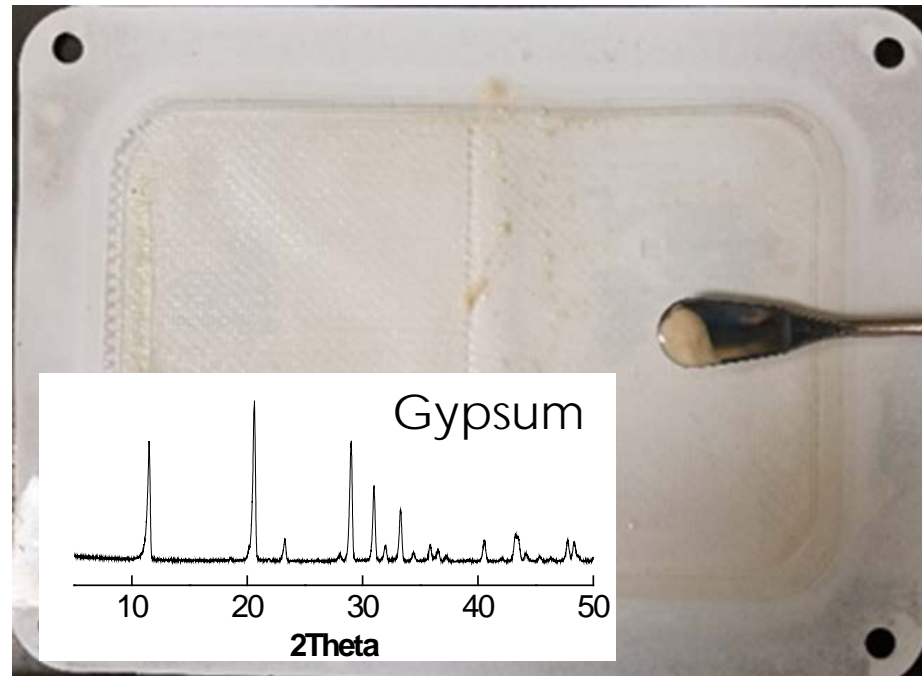
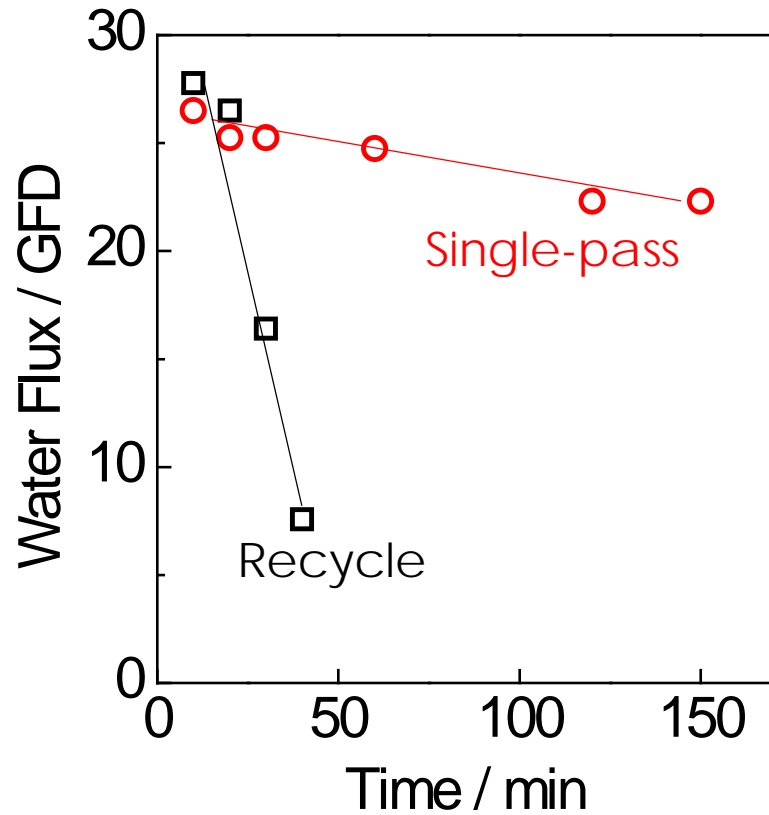
- For an EC unit, pre-concentrating Se can substantially reduce electricity consumption.

NF Setup: Materials Are Commercially Available.



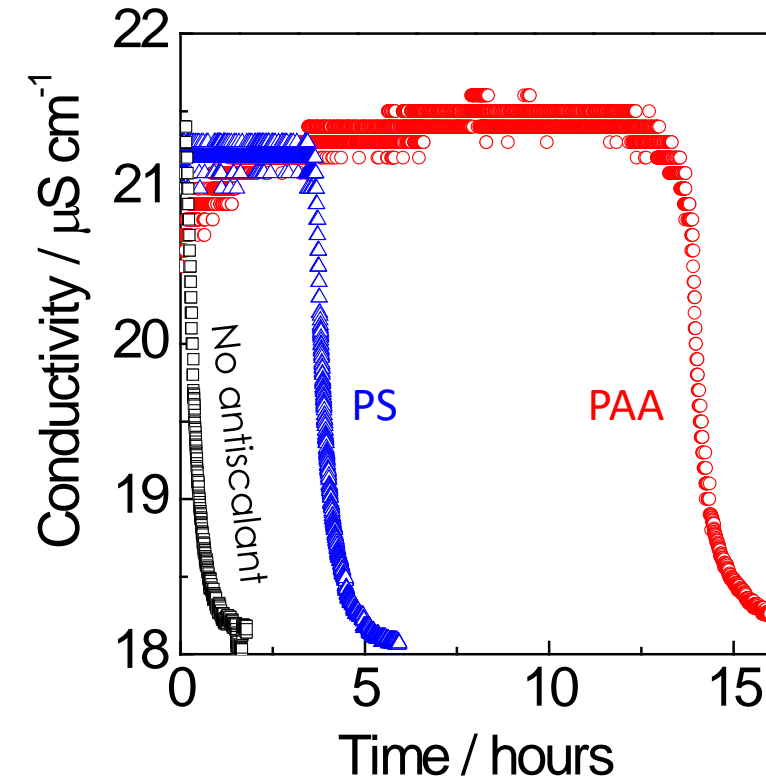
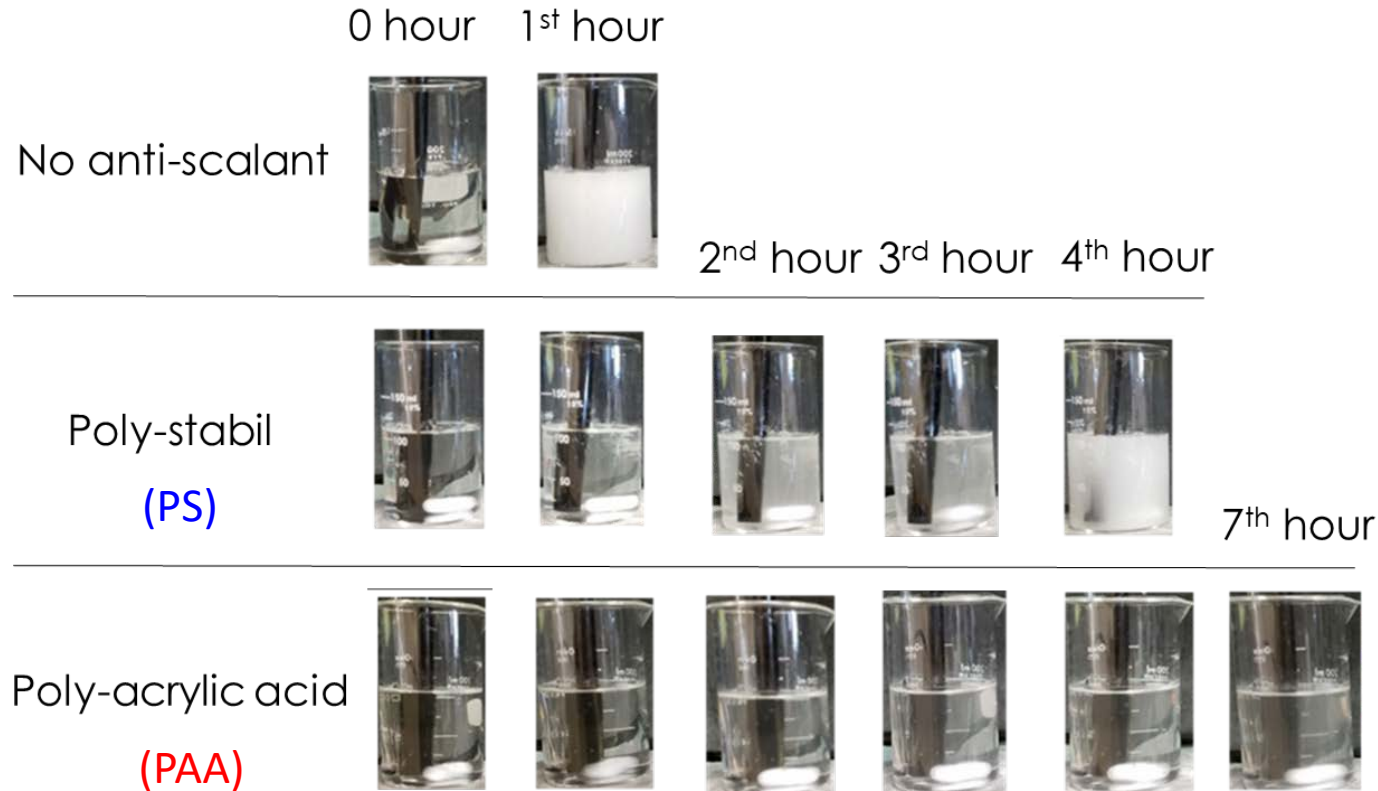
- Investigating TS80 membrane with enhanced Cl^- removal.
- NF performance with anti-salant.
- Operational pressure at 500 psig, and flow rate at 20 mL min^{-1} .

NF Cannot Sustain Performance Due to Gypsum Clogging.



- One-stage operation, 20 mL min^{-1} , 90% salt rejection, 0.014 m^2 .

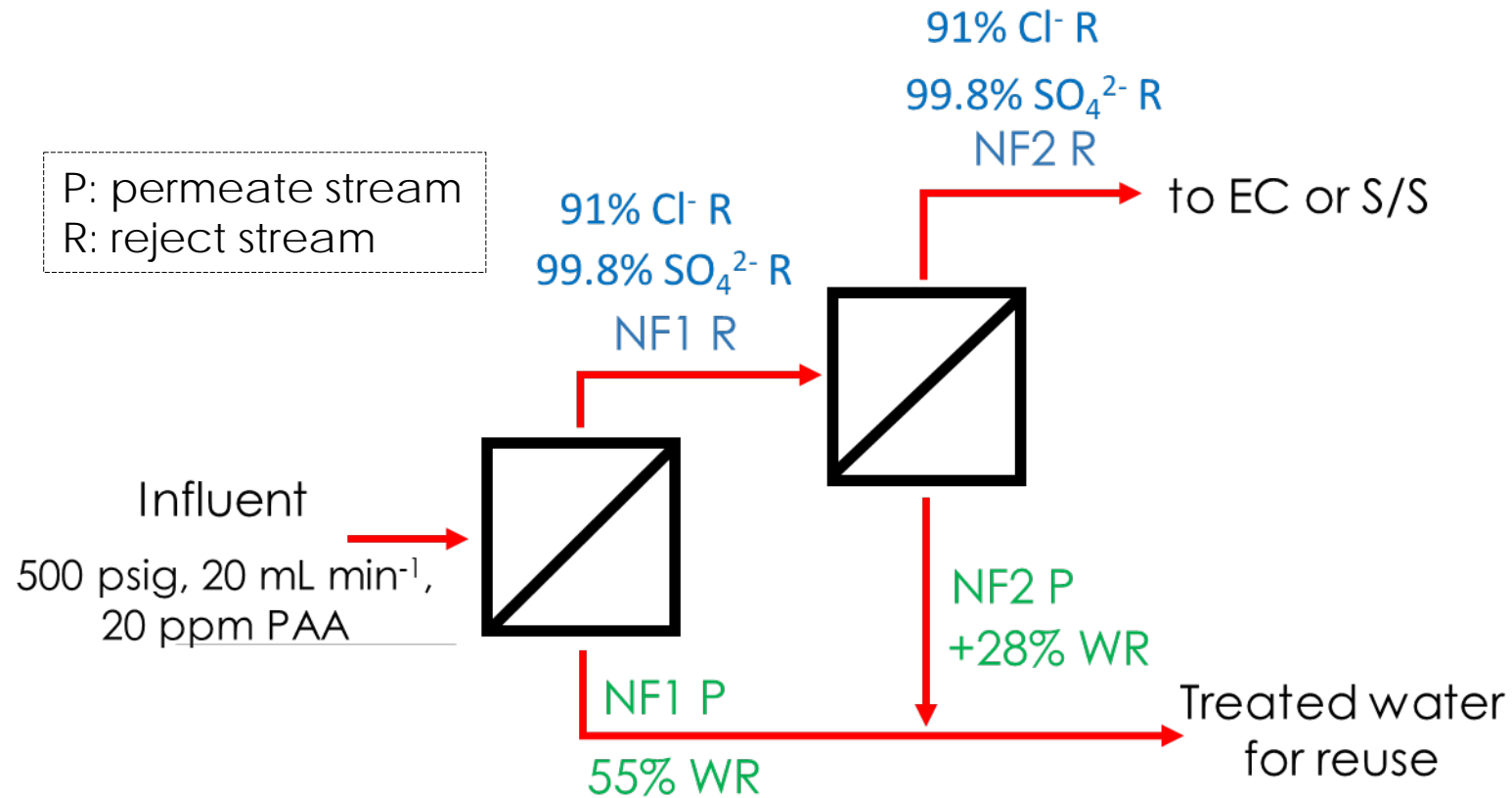
Mitigate of Gypsum Formation Using Antiscalant



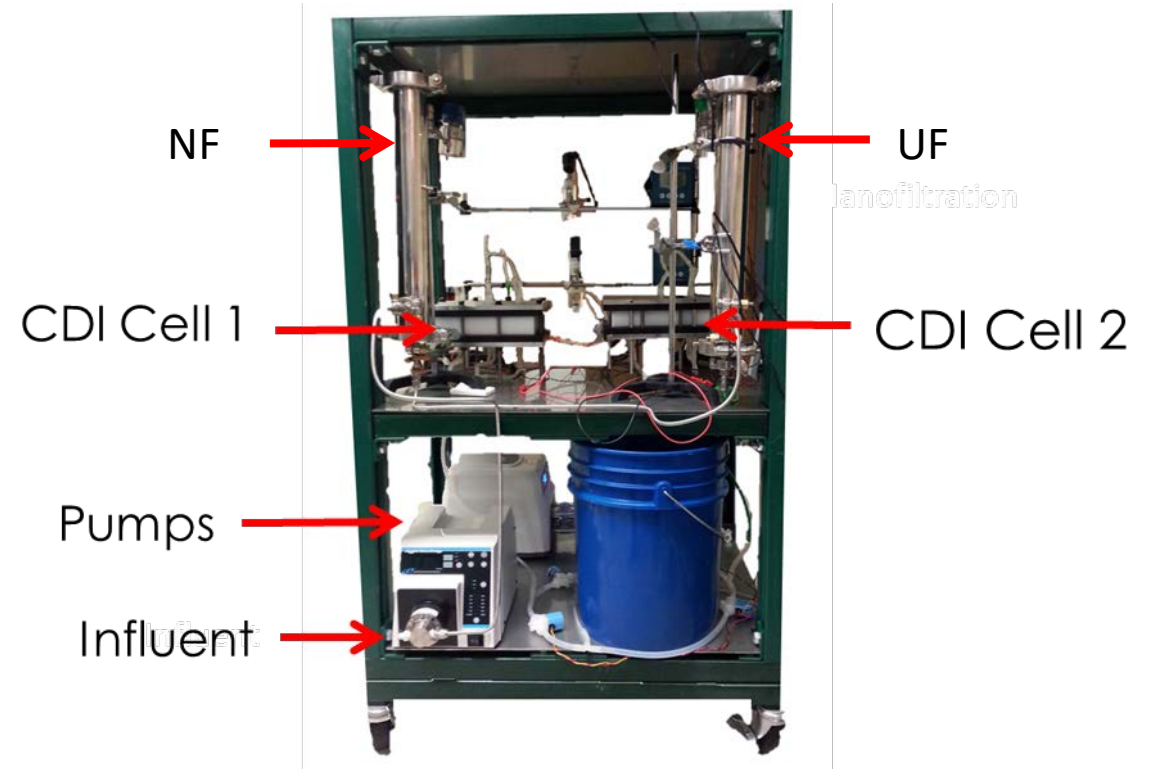
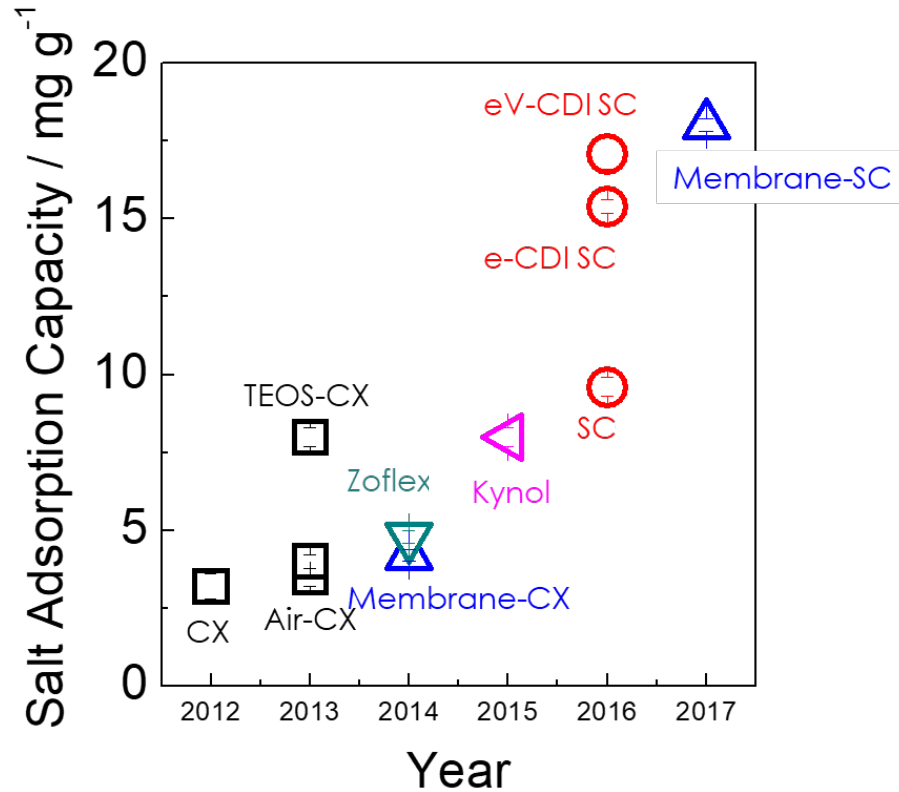
- Adding Na_2SO_4 and CaCl_2 into FGD water with 2.5 ppm anti-scalant.

- 2.5 ppm PAA extends induction time up to ~12 hours.

Two-Stage NF to Minimize the Discharge

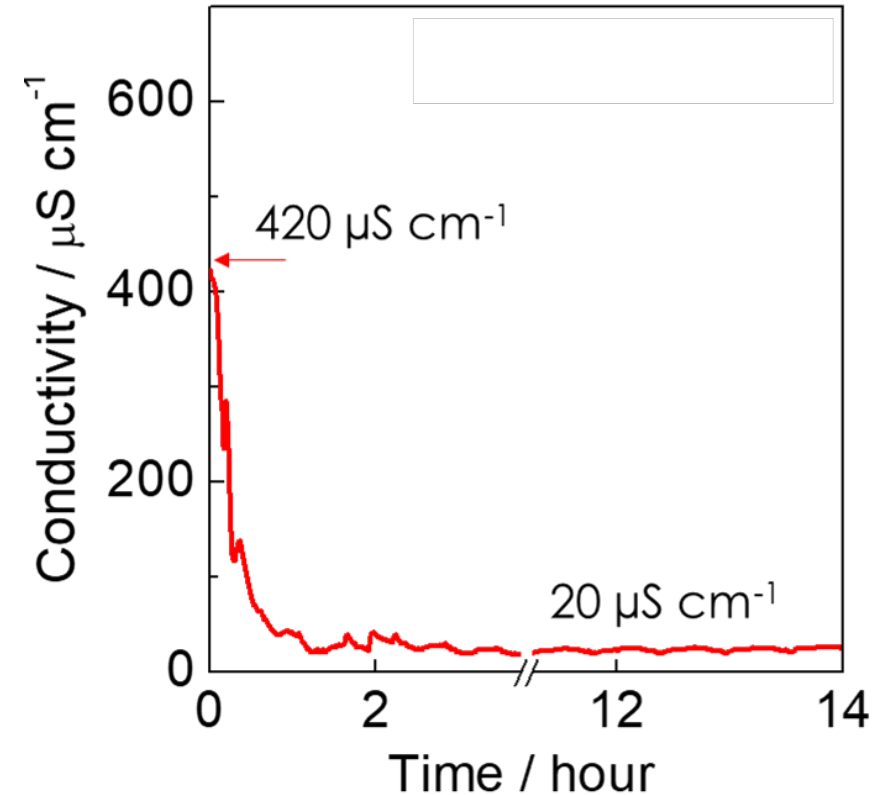
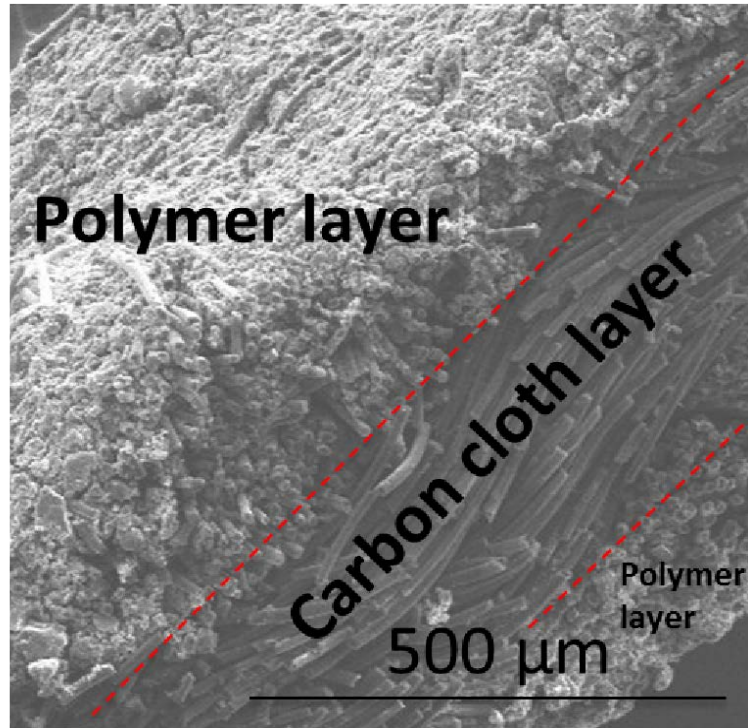


- Overall: 83% water recovery (WR), 88% Cl⁻ rejection, and 99.7% SO₄²⁻ rejection.



- Improved salt adsorption capacity by modifying carbon physical-chemical properties.

- Continuous CDI process integrated with membrane-based filtration.

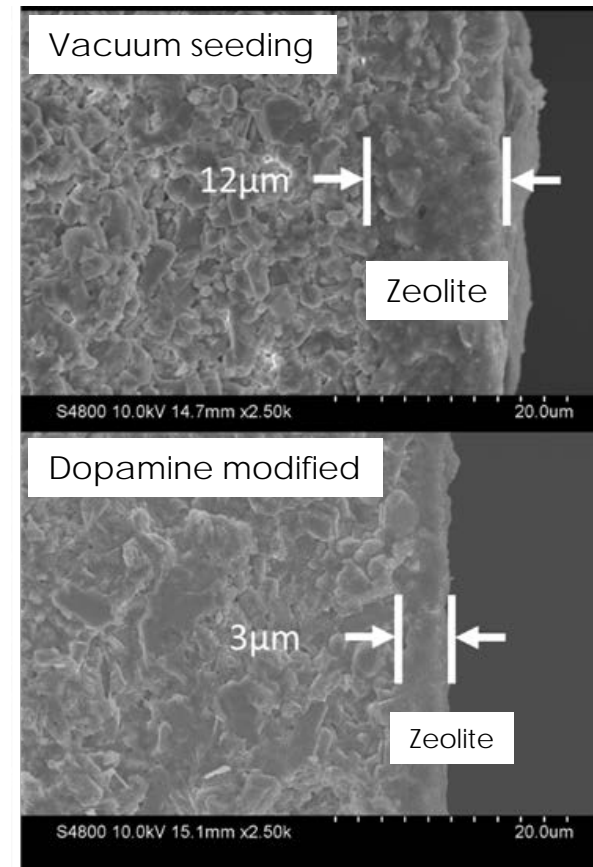


- Enhancing electrode's chemical surface charge and stability.

- Continuous operation at 1.4 V as a polishing step.

Zeolite: Excellent Salt Removal and Flux Improvements

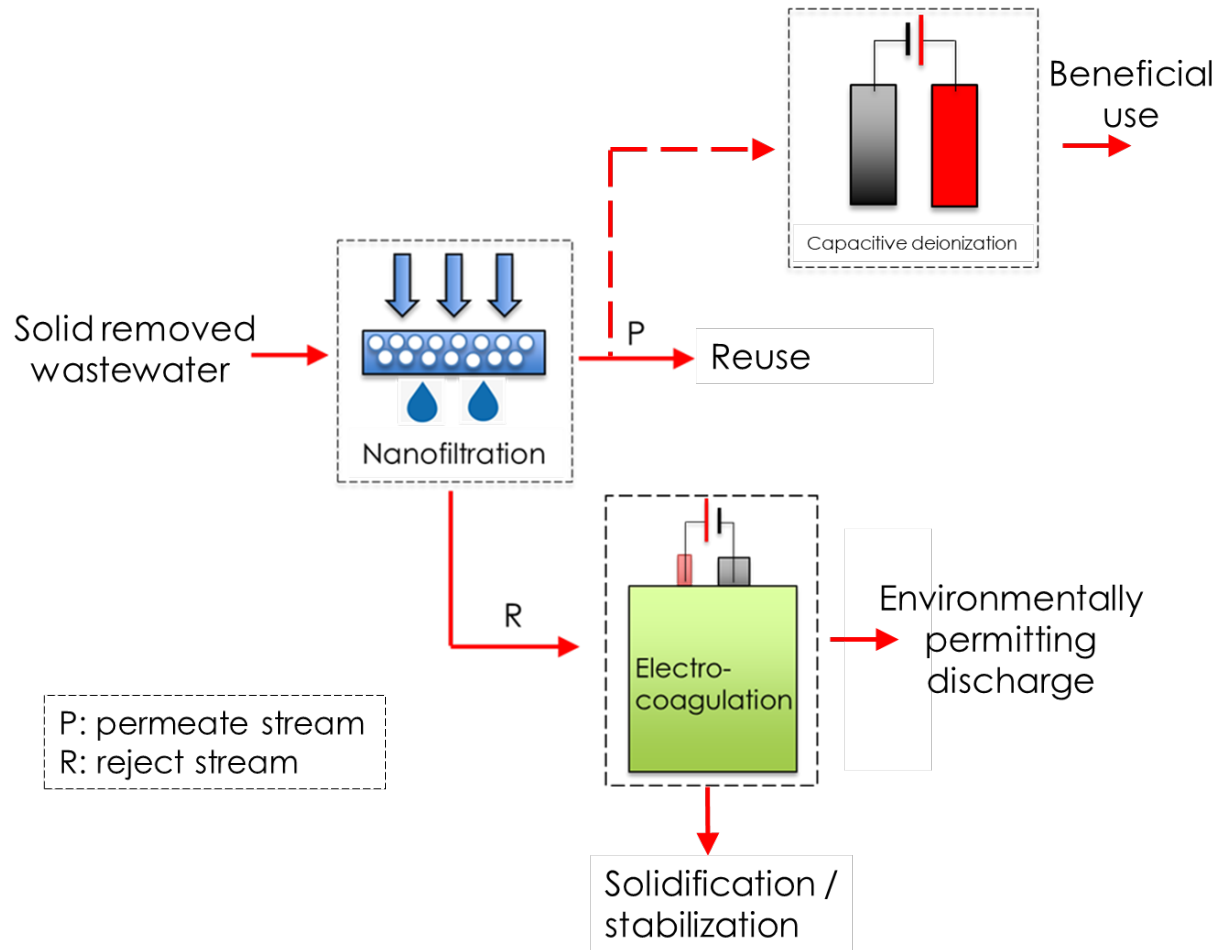
Species	NF reject / ppm	Permeate / ppm
Na	50.9 (1.3)	6.4 (0.4)
K	47.1 (0.7)	0
Mg	4,785.1 (28.1)	0
Ca	997.6 (1.3)	0
F	161.4 (12.5)	2.3 (0.1)
Cl	3,996.2 (16.5)	13.0 (0.1)
SO ₄ ²⁻	11,382.2 (381.2)	0
NO ₃ ⁻	293.0 (15.1)	0



- Reducing the thickness of zeolite membranes, modulating zeolite membranes, and mildly elevated temperature.

- At end of 2017, **789** coal-based power generation units with **279.2 GWe** capacity were in service.
- By 2040, **60% of electricity** in Kentucky will still be generated by **coal combustion**.
 - **1 MWh of electricity** generated by coal consumes about **700 gallons of water** as well as produces several process streams containing environmentally harmful species.
- Additional equipment such as **CO₂ capture units** can increase water consumption by approximately **23%**.
- **Water** is also needed to produce valuable chemicals through **coal gasification**.

Identified technologies



- Increasing treatment capability
 - Bench to pilot
 - Onsite demonstration
 - Utility and government supports
- Nanofiltration
 - Original equipment manufacturer to address precipitation issue
 - Softening
- Electrocoagulation
 - Improving solid-liquid separation
 - Reducing electricity consumption

Concluding Remarks

- EC reduced regulated species below the discharge limits.
- Two-stage NF showed >90% salt rejection and >80% water recovery.
- CDI is ready to be deployed as a polishing step.
- Zeolite possessed an effective salt rejection.

Acknowledgement



- Barbara Carney and Briggs White @ DOE/NETL
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